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SYNTHESIS OF $LaCoO_3$ FROM LANTHANUM TRISOXALATOCOBALTATE(III) (LTC) PRECURSOR EMPLOYING MICROWAVE HEATING TECHNIQUE

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Abstract

Lanthanum cobaltite $LaCoO_3$, an important catalyst and an electronic material used as cathode in solid oxide fuel cells was prepared from lanthanum trisoxalatocobaltate(III) hydrate $[LaCo(C_2O_4)_3]\cdot 9H_2O$ (LTC) employing microwave heating technique. It was observed that LTC heated in microwave heating system gives a pure product of $LaCoO_3$ at 400°C within one hour. Thermogravimetry, differential thermal analysis and X-ray diffraction techniques were used to optimize conditions for microwave processing of the precursor.

Keywords: catalyst, $LaCoO_3$, microwave heating, solid oxide fuel cells

Introduction

Pure and doped lanthanum cobaltites have potential applications as catalysts for hydrocarbon oxidation [1, 2]. Libby [3] showed the possible utility of rare earth cobaltites $LnCoO_3$ (*Ln*=rare earths) as autoexhaust catalysts. It has been reported [4] that this class of compounds act as active catalysts for the oxidation of carbon monoxide in autoexhaust. Meadowcraft [5] suggested that $LaCoO_3$ could be used as a good solid oxide fuel cell (SOFC) material. Shimizu and coworkers [6] showed that $LaCoO_3$ doped with Ca could be used as an electrode material for rechargeable metal air battery.

Different methods of preparation of $LaCoO_3$ are reported in the literature. Aksham *et al*. [7] prepared $LaCoO_3$ for the first time by heating a mixture of hexahydrate of lanthanum and cobalt nitrate above 800°C for a long period (>12 h). Gallagher [8] prepared this material by thermal decomposition of $LaCo(CN)_6\cdot 5H_2O$. Nag and Roy [9] reported that rare earth trisoxalatocobaltates(III) ideally serve as precursors for the synthesis of $LnCoO_3$. $LaCoO_3$ could also be prepared from coprecipitated carbonates, hydroxides, citrates, etc. and followed by calcination at different temperatures [10].

In our previous communication [11], we have shown that the microwave technique can be effectively used to bring down the temperature and time for the synthe-

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sis of $BaTiO_3$ powder. In this paper, we show that it is possible to apply similar method for the synthesis of $LaCoO_3$. In the present work we report the synthesis of $LaCoO_3$ from lanthanum trisoxalatocobaltate(III) hydrate (LTC), employing microwave-heating technique.

Prior knowledge of thermal behavior of the precursor is essential in the selection of temperature for the synthesis of desired compound from it in microwave system. Thermal techniques like TG and DTA can be successfully employed in arriving at this temperature [12–15].

Experimental

Materials

Lanthanum nitrate $La(NO_3)_3 \cdot 6H_2O$ (LN) used for synthesis, was of AR grade and procured from Thomas Baker Limited, Mumbai, India. Potassium trisoxalatocobaltate(III) hydrate $K_3Co(C_2O_4)_3 \cdot 4H_2O$ (KTC) was prepared by the method discussed in [16]. LTC was prepared from aqueous solutions of LN and KTC. 2 M aqueous solution of LN was added to the 2 M aqueous solution of KTC with constant stirring. The mixture was cooled in ice, filtered and the precipitate was first washed with small portion of ice-cold water, then with acetone and finally dried in air. The green compound formed was chemically analysed and assigned the formula $LaCo(C_2O_4)_3 \cdot 9H_2O$.

Thermogravimetry (TG) and differential thermal analysis (DTA)

The TG curve of LTC was recorded on 60.8 mg of sample in static air at a heating rate 10°C min^{-1} using the thermogravimetric balance designed and fabricated from indigenously available components. In addition, DTA plot for the decomposition of LTC was recorded in static air at a heating rate of 10°C min^{-1}, using the instrument supplied by Universal Thermal Analysis Instruments, Mumbai built to our specifications.

Synthesis of lanthanum cobaltite $LaCoO_3$

Lanthanum cobaltite was prepared by heating LTC in silicon carbide furnace as well as in microwave heating system. LTC was heated in silicon carbide furnace at 800°C for one hour. Also LTC was heated in microwave heating system in the temperature range of 400 to 800°C with interval of 100°C for the same period. The product obtained after heat treatment at different temperatures was analysed by X-ray diffraction using X-ray diffractometer (Siemens, Model D-500) at the scanning rate of 1° 2θ min^{-1}, using monochromatised X-ray beam of wavelength 0.15405 nm.

Results and discussion

The TG curve recorded for the LTC is shown in Fig. 1. The TG curve indicates that LTC decomposes in three steps involving dehydration and decarboxylation to give $LaCoO_3$ as the final product. DTA curve of LTC recorded in static air is represented in

Fig. 2. DTA curve shows that LTC decomposes in different steps involving dehydration and decarboxylation yielding final product above 670°C. The first endothermic peak in DTA located around 145°C is due to dehydration followed by decarboxylation (~200°C) of LTC indicated by Eq. (1). The evolution of H_2O and CO_2 however cannot be delineated due to partial overlap of the two peaks. These two superimposing endothermic peaks are followed by apparently exothermic peaks observed in the temperature range 250 to 445°C, which could have resulted by superimposition of an endothermic peak due to decomposition of carboxylate and simultaneous oxidation of evolved CO (reaction 2) to CO_2 in air. Finally, a small endotherm is observed at 670°C indicating the formation of $LaCoO_3$ phase according to reaction 3.

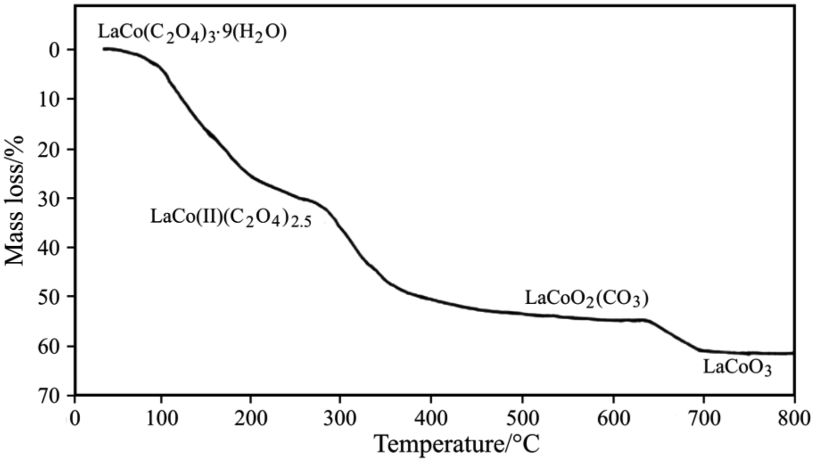

Fig. 1 TG curve of LTC recorded in static air

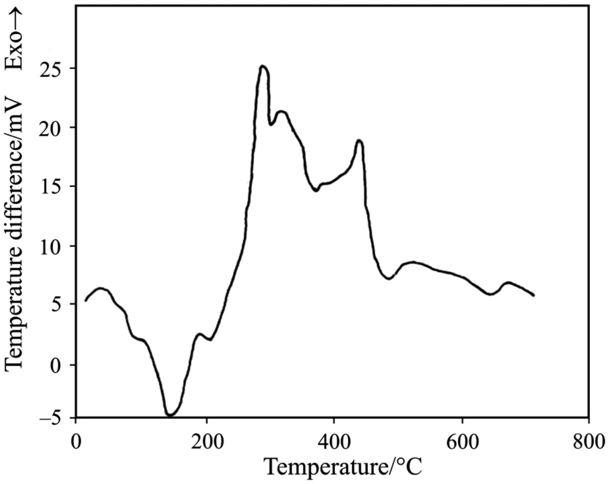

Fig. 2 DTA plot of LTC recorded in static air

From TG and DTA study we suggest the mechanism for thermal decomposition of LTC as

$$LaCo(C_2O_4)_3\cdot 9(H_2O)\rightarrow LaCo(II)(C_2O_4)_{2.5}+CO_2+9(H_2O) \quad (1)$$

$$LaCo(II)(C_2O_4)_{2.5}\rightarrow LaCoO_2(CO_3)+CO_2+3CO \quad (2)$$

$$LaCoO_2(CO_3)\rightarrow LaCoO_3+CO_2 \quad (3)$$

The decomposition mechanism presented here based on the TG and DTA data is in good agreement with the mechanism reported by Kutty *et al*. [17] and leads to the conclusion that $LaCoO_3$ is formed from LTC above 670°C. This information is obviously useful in choosing the calcination temperature to get $LaCoO_3$ from LTC.

XRD patterns

The X-ray diffraction patterns of LTC calcined in silicon carbide furnace at 800°C and LTC calcined in microwave heating system at 400 and 800°C are shown in Fig. 3. XRD pattern of LTC calcined in silicon carbide furnace at 800°C for 1 h (Fig. 3a) showed the formation of the mixture of $LaCoO_3$, La_2O_3, CoO, Co_3O_4 and some unidentified phase, which could be lanthanum carbonate formed by the interaction of La_2O_3 resulting from decomposition of LTC. La_2O_3 is known to react with moisture and CO_2 in atmosphere forming lanthanum carbonate. But the LTC calcined in microwave heating system at temperature as low as 400°C for one hour (Fig. 3b) showed the formation of pure $LaCoO_3$. The X-ray diffraction pattern of the product formed at 400°C was in close agreement with that of rhombohedral structure of

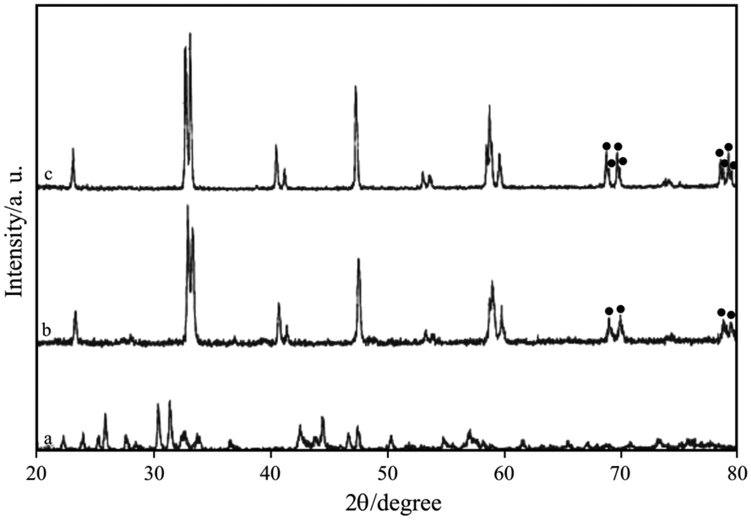

Fig. 3 XRD patterns of LTC calcined in silicon carbide furnace at a – 800°C for 1 h and LTC calcined in microwave heating system at b – 400°C and c – 800°C for 1 h (● – indicates the splitting of lines in c)

$LaCoO_3$ reported in [7, 18]. The product formed after calcination of LTC in microwave heating system at 500 and 600°C was found to have the same structure but was more crystalline in nature. However, the product obtained after calcination of LTC in microwave heating system above 700°C showed splitting of some higher angle (>60° 2θ) lines in XRD-pattern (Fig. 3c), indicating the possibility of phase transformation of product from one phase to another, the two phases being closely related to each other crystallographically. Raccah and Goodenough [19] and Bhide *et al*. [20] have observed the first order phase transition in this material attributed to localized to collective electron behavior at 927±10°C. It is possible that the temperature of this transition (~800°C) is lowered by the presence of the microwave field, as observed in the present investigation.

$LaCoO_3$ is used as a catalyst for oxidation of hydrocarbons [1, 2] as well as carbon monoxide [4, 5] in autoexhaust. Catalytic activity in addition to other factors also depends on the particle size. Small particle size material is more effective for catalytic activity. The temperature 400°C, at which the present sample is prepared by this method is sufficiently low to yield material of very small particle size. The surface area of the $LaCoO_3$ prepared in the present work, determined by BET gas adsorption technique was found to be $3.2\ m^2\ g^{-1}$.

Conclusions

Synthesis of $LaCoO_3$ reported by earlier investigators [7, 9, 10] required high temperature (>800°C) and long heating periods (more than 12 h). We adopted a new method in which LTC was heated at 800°C in silicon carbide furnace for 1 h and in microwave heating system in the temperature range 400–800°C for the same period. It is observed that LTC when heated in microwave heating system yields pure rhombohedral $LaCoO_3$ at 400°C within one hour. On the contrary, the same material heated in silicon carbide furnace at 800°C for one hour in our experiments barely showed the formation of $LaCoO_3$. These observations indicate that the microwave heating facilitates the formation of $LaCoO_3$ from LTC precursor at much lower temperatures.

It can be concluded from the present work that the microwave assisted technique adopted for the synthesis of $LaCoO_3$ is superior compared to the other methods, from the point of view of energy and time saving.

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